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STRUCTURE AND PROPERTIES OF INORGANIC SOLIDS

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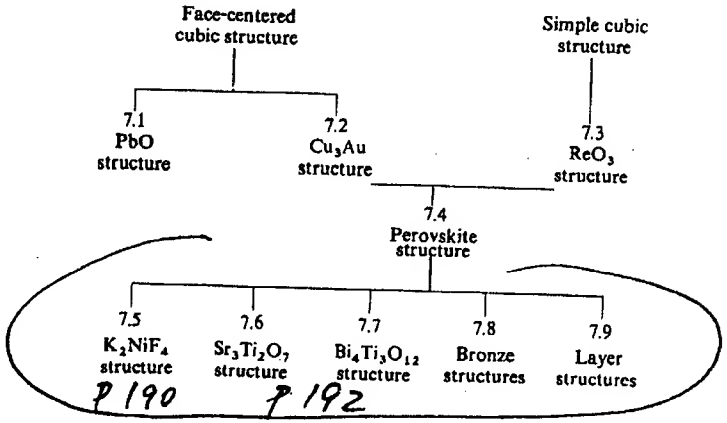
CHAPTER 7

PEROVSKITE TYPE AND RELATED STRUCTURES

THE perovskite-type structures are formed by ABX_3-type compounds where the A atoms replace some of the X atoms in close-packed cubic layers and the B atoms fit in the octahedrally coordinated sites. In the ordered Cu_3Au structure there are no B atoms; in the ReO_3 structure the A atoms are missing so that there are holes in the close-packed X atom layers. These close-packed layers are perpendicular to the ⟨111⟩ directions (body diagonals) in the cubic unit cell. Related structures can be built up as close-packed layers of X atoms or by stacking cubic unit cells. The flow diagram showing the relationships between these structures is presented in Table 7.0.

TABLE 7.0.



7.1. Red Lead Oxide, PbO, B10, *P4/pmm*, Tetragonal

This lead oxide structure can be visualized by starting with an ordered cubic close-packed structure. Lead atoms are placed in the centered positions on the vertical faces of a unit cell and the oxygen atoms in the centered position on the top and bottom faces as well as at the cell corners. The cubic

cell is elongated in the c direction; the lead atoms are displaced vertically downwards in the front and back faces and upwards in the side faces. This arrangement corresponds to placement of the atoms in the following special positions in space group $P4/nmm$:

$$2\text{Pb at (2c)}: 0, \tfrac{1}{2}, z; \tfrac{1}{2}, 0, \bar{z} \text{ with } z = 0.2385;$$
$$2\text{O at (2a)}: 0, 0, 0; \tfrac{1}{2}, \tfrac{1}{2}, 0.$$

In this structure both the lead and oxygen atoms are in fourfold coordination with atoms of the other type. The oxygen atoms are in a tetrahedron of lead atoms, while the lead atoms are at the vertex of a square pyramid with oxygen atoms at the base. In the horizontal oxygen sheets, the atoms are in square planar coordination or roughly cubic packing. This structure is illustrated in Fig. 7.1. Other compounds which adopt this structure are listed in Table 7.1.

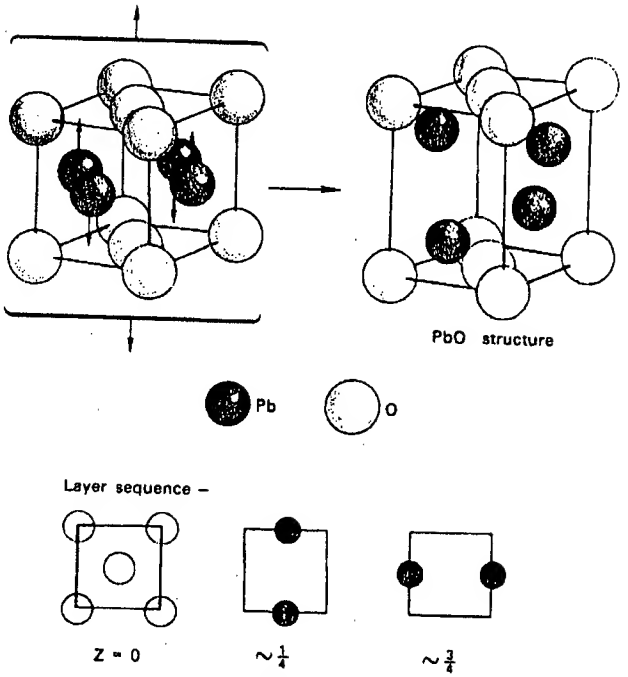


FIG. 7.1 Lead oxide structure

TABLE 7.5. *Phases with the K_2NiF_4 Structure*

Phases	Cell size (Å)		Atomic parameters		Refs.
	a_0	c_0	z(A cation)	z(anion)	
Halides, Oxyhalides					
Cs_2CrCl_4	5.215	16.46			1
K_2CoF_4	4.074	13.08			2
K_2CuF_4	4.155	12.74	0.356	0.153	3
K_2MgF_4	3.977	13.16	0.35	0.15	4
K_2NiF_4	4.01	13.08	0.352	0.151	5
K_2NbO_3F	3.96	13.67			6
K_2ZnF_4	4.017	13.05			7
$(NH_4)_2NiF_4$	4.084	13.79			8
Rb_2NiF_4	4.087	13.71			8
Rb_2ZnF_4	4.104	13.28			7
Sr_2FeO_3F	3.84	12.98			9
Tl_2CoF_4	4.10	14.1			2
Tl_2NiF_4	4.051	14.22			8
Oxides					
Ba_2PbO_4	4.296	13.30	0.355	0.155	10
Ba_2SnO_4	4.130	13.27	0.355	0.155	10
Ca_2MnO_4	3.67	12.08			11
Cs_2UO_4	4.38	14.79			12
Gd_2CuO_4	3.89	11.85			13
K_2UO_4	4.34	13.10	0.36	0.145	14
La_2NiO_4	3.855	12.652	0.360	1.170	15
Nd_2CuO_4	3.94	12.15			13
Nd_2NiO_4	3.81	12.31			13
Rb_2UO_4	4.345	13.83			12
Sm_2CuO_4	3.91	11.93			13
Sr_2IrO_4	3.89	12.92	0.347	0.151	16
Sr_2MnO_4	3.79	12.43			5
Sr_2MoO_4	3.92	12.84			5
Sr_2RhO_4	3.85	12.90			17
Sr_2RuO_4	3.870	12.74			17
Sr_2SnO_4	4.037	12.53	0.353	0.153	10
Sr_2TiO_4	3.884	12.60	0.355	0.152	18
Complex Oxides					
$La_2(Li_{0.5}Co_{0.5})O_4$	3.77	12.58			19
$La_2(Li_{0.5}Ni_{0.5})O_4$	3.75	12.89			19
$SrLaAlO_4$	3.75	12.5			11
$SrLaCoO_4$	3.80	12.50			19
$(Sr_{1.5}La_{0.5})(Co_{0.5}Ti_{0.5})O_4$	3.85	12.62			19
$SrLaCrO_4$	3.84	12.52			19
$(Sr_{0.5}La_{1.5})(Mg_{0.5}Co_{0.5})O_4$	3.82	12.58			19
$SrLaFeO_4$	3.86	12.69			19
$SrLaGaO_4$	3.84	12.71			19
$SrLaMnO_4$	3.88	12.5			19
$SrLaNiO_4$	3.80	12.51			19
$SrLaRhO_4$	3.92	12.78			19

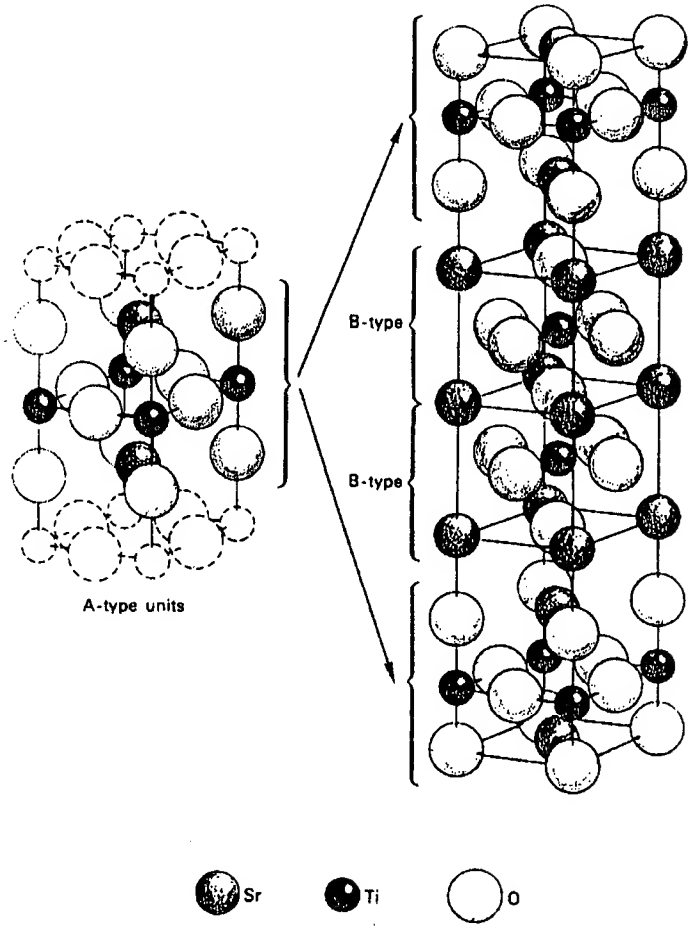


FIG. 7.6 The $Sr_3Ti_2O_7$ structure

The structure of $Sr_4Ti_3O_{10}$ is similar but requires a longer c-axis to describe it. The cell sizes are listed in Table 7.6.

TABLE 7.6. *Series of* Sr–Ti–O *Compounds*

Compound	Cell size (Å)		Refs.
	a_0	c_0	
Sr_2TiO_4	3.884	12.60	1
$Sr_3Ti_2O_7$	3.90	20.38	2
$Sr_4Ti_3O_{10}$	3.90	28.1	2
$K_3Zn_2F_7$	4.063	21.22	3

7.7. $Bi_4Ti_3O_{12}$ Structure, *Fmmm*, Orthorhombic

$Bi_4Ti_3O_{12}$ is one of a series of ferroelectric compounds which can be best described by unit cells of the perovskite structure stacked on one another and separated by bismuth oxygen layers. The structures of Bi_2NbO_5F, Bi_3NbTiO_9 and $BaBi_4TiO_{15}$ have been characterized, but in this book, only one, $Bi_4Ti_3O_{12}$, will be described. Half the unit cell consists of one and one-half A type perovskite unit cells with an oxygen layer on top and one and one-half B type perovskite unit cells on top of the oxygen layer. The top half of the cell is the mirror image of this one. The unit cell just described is shown in Fig. 7.7a inside the real cell. The actual a and b edges are taken as the face diagonals of the small unit cell of the perovskite structure. The layer sequence is shown in Fig. 7.7b. The atomic positions are given below:

		x	y	z
Bi(1)	(8i)	0	0	0.067
(2)	(8i)	0	0	0.211
Ti(1)	(4b)	0	0	0.50
(2)	(8i)	0	0	0.372
O(1)	(8e)	0.25	0.25	0
(2)	(8f)	0.25	0.25	0.25
(3)	(8i)	0	0	0.436
(4)	(8i)	0	0	0.308
(5)	(16j)	0.25	0.25	0.128

(4b) $0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0$

(8e) $\frac{1}{4}, \frac{1}{4}, 0; \frac{1}{4}, \frac{1}{4}, \frac{1}{2}$
$\frac{3}{4}, \frac{3}{4}, 0; \frac{3}{4}, \frac{3}{4}, \frac{1}{2}$
$\frac{3}{4}, \frac{1}{4}, \frac{1}{2}; \frac{3}{4}, \frac{1}{4}, 0$
$\frac{1}{4}, \frac{3}{4}, \frac{1}{2}; \frac{1}{4}, \frac{3}{4}, 0$

(8f) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{1}{4}, \frac{3}{4}$
$\frac{3}{4}, \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4}$
$\frac{3}{4}, \frac{1}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4}, \frac{1}{4}$
$\frac{1}{4}, \frac{3}{4}, \frac{3}{4}; \frac{1}{4}, \frac{3}{4}, \frac{1}{4}$

(8i) $0, 0, z; \frac{1}{2}, \frac{1}{2}, z; \frac{1}{2}, 0, \frac{1}{2} + z; 0, \frac{1}{2}, \frac{1}{2} + z$
$0, 0, z; \frac{1}{2}, \frac{1}{2}, z; \frac{1}{2}, 0, \frac{1}{2} - z; 0, \frac{1}{2}, \frac{1}{2} - z$

(16j) $\frac{1}{4}, \frac{1}{4}, z; \frac{1}{4}, \frac{1}{4}, \bar{z}; \frac{1}{4}, \frac{3}{4}, z; \frac{1}{4}, \frac{3}{4}, \bar{z}$
$\frac{3}{4}, \frac{3}{4}, z; \frac{3}{4}, \frac{3}{4}, \bar{z}; \frac{3}{4}, \frac{1}{4}, z; \frac{3}{4}, \frac{1}{4}, \bar{z}$
$\frac{3}{4}, \frac{1}{4}, \frac{1}{2} + z; \frac{3}{4}, \frac{1}{4}, \frac{1}{2} - z; \frac{3}{4}, \frac{3}{4}, \frac{1}{2} + z; \frac{3}{4}, \frac{3}{4}, \frac{1}{2} - z$
$\frac{1}{4}, \frac{3}{4}, \frac{1}{2} + z; \frac{1}{4}, \frac{3}{4}, \frac{1}{2} - z; \frac{1}{4}, \frac{1}{4}, \frac{1}{2} + z; \frac{1}{4}, \frac{1}{4}, \frac{1}{2} - z$

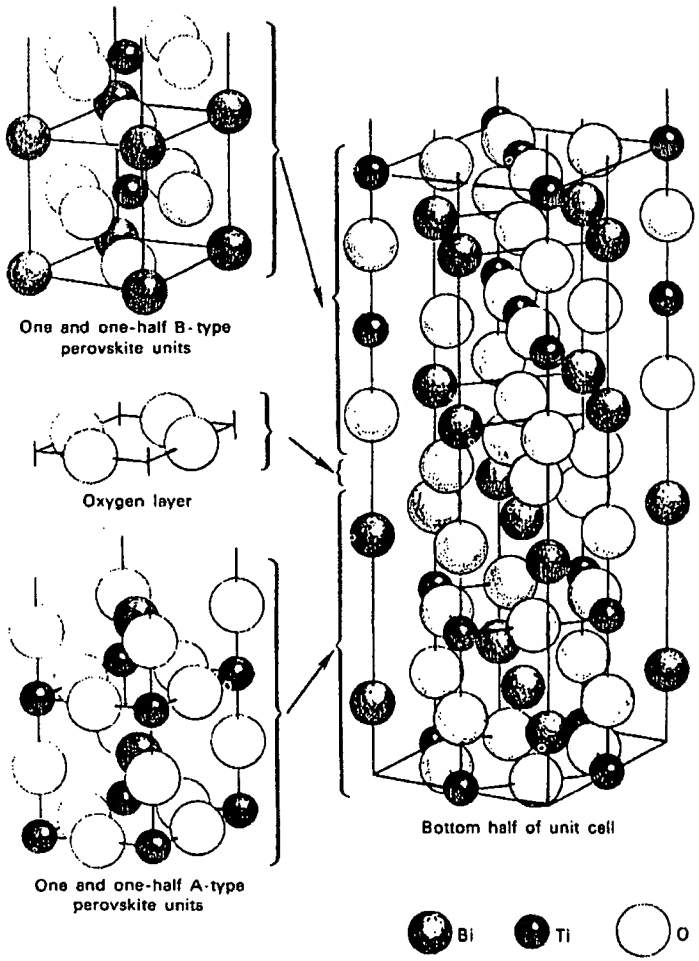


FIG. 7.7a The $Bi_4Ti_3O_{12}$ structure (one-half the unit cell)